

Study finding perchlorate in fertilizer rattles industry

Preliminary findings by an EPA research laboratory published in this issue of *ES&T* (pp. 3469-3472) indicate that commonly available garden fertilizers contain perchlorate concentrations ranging from 0.15% to 0.84% by weight. The report prompted harsh and immediate denunciations from the fertilizer producers' trade group.



Perchlorate in fertilizers may accumulate in crops, such as this lettuce growing in an irrigated field in the southwestern United States. (Agricultural Research Service, USDA)

The findings of the study, "Perchlorate Identification in Fertilizers," by Sridhar Susarla and coworkers, add an additional dimension to the emerging picture of perchlorate contamination. Perchlorate, ClO_4 , has been found in groundwater, drinking water, and soils, mainly in the southwestern United States at levels that range from 8 to 3700 parts per billion (ppb). The highest levels come from wells located near ammonium perchlorate manufacturer Kerr-McGee Chemical Corp., located in Henderson, Nev. The primary source of contamination appears to be industrial and military operations that use perchlorate as an oxidizing agent (*ES&T* 1998, 32 (9), 210A).

Perchlorate is an unregulated contaminant, although in 1997, California adopted an advisory level of 18 ppb in drinking water. EPA's draft reference dose, currently under revision, leads to an advisory level of 32 ppb in drinking water (*ES&T* 1999, 33 (5), 110A-111A). But while the reference dose is being revised, EPA recommends a more conservative approach that aims for an advisory level of 4 to 18 ppb, according to Michael Osinski, at EPA's Office of Ground Water and Drinking Water. Perchlorate affects the thyroid and the production of thyroid hormones by blocking iodine uptake. These effects can cause mental retardation in unborn children and infants and thyroid tumors.

But the fertilizer perchlorate concentration values reported by Susarla and

coworkers at the EPA National Exposure Research Laboratory in Athens, Ga., are disputed by the fertilizer industry and are being questioned by some chemists familiar with the analytical problems presented by perchlorate. The Fertilizer Institute (TFI), a trade organization representing fertilizer manufacturers, in Washington, D.C., labeled the report "flawed, speculative, and premature." Edward Urbansky, an analytical chemist at EPA's National Risk Management Research Laboratory in Cincinnati, Ohio, said the results should be treated with caution because they suggest that perchlorate is much more ubiquitous than seems reasonable.

But other government and industry laboratories have also found perchlorate in a wide range of fertilizers, according to David Tsui, at the Operational Toxicology Branch, Wright Patterson Air Force Base, in Dayton, Ohio. Tsui is coordinating a round-robin analysis of fertilizers expected to be finalized this fall. The analysis is funded by the Perchlorate Study Group, a coalition of aerospace, defense, chemical, and other industries that use or manufacture perchlorate.

Perchlorate levels vary dramatically between fertilizers and between production lots, indicating that there are either differences in raw materials or production methods, said EPA toxicologist Annie Jarabek, speaking about the other analyses of perchlorate in fertilizer. Jarabek, who is based at EPA's National Center for Environmental Assessment in Research Triangle Park, N.C., is the principal author of EPA's draft toxicological report on perchlorate.

Both Susarla's study and the round-robin study raise concerns that fertilizer could be a source of perchlorate contamination to groundwater or to vegetables such as lettuce, which bioaccumulate perchlorate, according to Kevin Mayer, EPA's Region IX coordinator for perchlorate issues. He added that preliminary monitoring results from some agricultural areas indicate that storing and handling fertilizer could be causing problems in some areas.

Laboratory experiments in which lettuce is grown in solutions containing perchlorate show that lettuce can accumulate up to 0.1% wet weight, according to results presented by Susarla at the American Chemical Society's annual meeting in New Orleans in August. But in more realistic greenhouse experiments in which fertilizer is the source of perchlorate, lettuce accumulates up to 0.001% wet weight, according to the results of preliminary uptake studies presented by Stacy Lewis, also from EPA's Athens, Ga., laboratory, at the ACS meeting.

To check their results, Susarla's team used three analytical techniques: ion chromatography, Raman spectroscopy, and capillary electrophoresis. "We used three techniques to verify our results, because determining perchlorate concentrations in fertilizer is analytically challenging," said Susarla, the paper's corresponding author and a National Research Council fellow visiting the Athens laboratory.

But Ron Phillips, a spokesman for TFI, said that it was unable to reproduce any of the results reported in the *ES&T* research paper or in the round robin results.

In addition, Urbansky said the data raise many red flags, in part because the Athens researchers found perchlorate in samples of fertilizer components and

fertilizer where it would be unlikely—for example, in ammonium nitrate fertilizers that are created from atmospheric gases. Such raw ingredients cannot be contaminated with perchlorate. With such counterintuitive results, and at these relatively high concentrations (tenths of a percent) it would be easy and obvious to confirm the results using wet chemical methods, he said. Instead, the Athens researchers relied on techniques that do not produce a unique and definitive signature for perchlorate. These techniques can be confounded by other chemicals, he said.

However, Peter Jackson, an analytical chemist with Dionex Corp., a manufacturer of ion chromatographs in Sunnyvale, Calif., said that since the perchlorate fertilizer results were confirmed by capillary electrophoresis (CE), the identification of perchlorate should be correct. This is because CE has a higher perchlorate detection limit than ion chromatography. "You'd really have to have bad luck to ID something by two different selection techniques and get it wrong," he said.

Because they found perchlorate to be ubiquitous in the small sample of fertilizers they considered, the Athens researchers suggest that some production treatment common to all fertilizers, such as oils used to keep the fertilizer dry or brine solution used to control acidity, could be the source of perchlorate contamination. "The president of The Fertilizer Institute suggested this to us," said Steve McCutcheon, who is directing the perchlorate research at the Athens laboratory. TFI denies that such processes could be responsible for perchlorate contamination of fertilizers, said Ron Phillips, a spokesperson for TFI.

Perchlorate has been known since the late 1800s to be a constituent of naturally occurring nitrate deposits in Chile. But Chilean nitrates are currently used in the United States in relatively small quantities, on specialized crops, mainly tobacco, cotton, fruits, and vegetables, according to Phillips. The United States uses 75,000 short tons of Chilean nitrate annually. Total annual fertilizer usage is 54 million short tons.

The finding of perchlorate in fertilizer and that some farms produce crops—in particular lettuce—that can bioaccumulate perchlorate means that there are additional exposure routes to consider in developing a risk assessment for perchlorate, according to Jarabek.

External peer reviewers of the draft toxicological report recommended studies of bioaccumulation in lettuce and measurements of perchlorate concentrations in fruits and vegetables from farms with perchlorate contamination, she said. Delays in receiving several million dollars in Department of Defense (DoD) funding to pay for these studies have caused holdups in revising the toxicological review, she said. This fall, EPA expects DoD to confirm that it will fund the studies and expects to have the toxicological review finished in the fall of 2000.

In the spring of 2000, a survey of perchlorate occurrences by the American Water Works Research Foundation is due. EPA is also preparing a new standard method (Number 309) for analyzing perchlorate in water, and the contaminant is to be added to the unregulated contaminant monitoring rule. This means that EPA regions and states will be required to monitor surface and groundwater for

perchlorate. —REBECCA RENNER

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